

What is claimed is:

1. A method of producing a nanoporous silica dielectric film comprising
(a) preparing a composition comprising a silicon containing pre-polymer, a
5 porogen, and a metal-ion-free catalyst selected from the group consisting of
onium compounds and nucleophiles;
(b) coating a substrate with the composition to form a film,
(c) crosslinking the composition to produce a gelled film, and
(d) heating the gelled film at a temperature and for a duration effective to
10 remove substantially all of said porogen.
2. The method of claim 1 wherein the nanoporous silica dielectric film has a
pore void volume of from about 5% to about 80% based on the volume of the
film.
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3. The method of claim 1 wherein the resulting nanoporous silica dielectric
film has a dielectric constant of about 3 or below.
4. The method of claim 1 wherein the nanoporous silica dielectric film has an
20 average pore diameter in the range of from about 1 nm to about 30 nm.
5. The method of claim 1 wherein the catalyst is selected from the group
consisting of ammonium compounds, amines, phosphonium compounds and
phosphine compounds.
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6. The method of claim 1 wherein the catalyst is selected from the group
consisting of tetraorganoammonium compounds and tetraorganophosphonium
compounds.

7. The method of claim 1 wherein the catalyst is selected from the group consisting of tetramethylammonium acetate, tetramethylammonium hydroxide, tetrabutylammonium acetate, triphenylamine, trioctylamine, tridodecylamine, triethanolamine, tetramethylphosphonium acetate, 5 tetramethylphosphonium hydroxide, triphenylphosphine, trimethylphosphine, trioctylphosphine, and combinations thereof.

8. The method of claim 1 wherein the composition further comprises a non-metallic, nucleophilic additive which accelerates the crosslinking of the 10 composition.

9. The method of claim 1 wherein the composition further comprises a nucleophilic additive which accelerates the crosslinking of the composition, which is selected from the group consisting of dimethyl sulfone, dimethyl 15 formamide, hexamethylphosphorous triamide, amines and combinations thereof.

10. The method of claim 1 wherein the composition further comprises water in a molar ratio of water to Si ranging from about 0.1:1 to about 50:1.

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11. The method of claim 1 wherein the composition comprises a silicon containing prepolymer of Formula I:



25 wherein x is an integer ranging from 0 to about 2, and y is x-4, an integer ranging from about 2 to about 4;

R is independently selected from the group consisting of alkyl, aryl, hydrogen, alkylene, arylene, and combinations thereof;

L is an electronegative moiety, independently selected from the group consisting of alkoxy, carboxyl, acetoxy, amino, amido, halide, isocyanato and combinations thereof.

5 12. The method of claim 11 wherein the composition comprises a polymer formed by condensing a prepolymer according to Formula I, wherein the number average molecular weight of said polymer ranges from about 150 to about 300,000 amu.

10 13. The method of claim 1 wherein the composition comprises a silicon containing pre-polymer selected from the group consisting of an acetoxysilane, an ethoxysilane, a methoxysilane, and combinations thereof.

14. The method of claim 1 wherein the composition comprises a silicon
15 containing pre-polymer selected from the group consisting of tetraacetoxysilane, a C₁ to about C₆ alkyl or aryl-triacetoxysilane, and combinations thereof.

15. The method of claim 14 wherein said triacetoxysilane is
20 methyltriacetoxysilane.

16. The method of claim 1 wherein the composition comprises a silicon
containing pre-polymer selected from the group consisting of tetrakis(2,2,2-
trifluoroethoxy)silane, tetrakis(trifluoroacetoxy)silane, tetraisocyanatosilane,
25 tris(2,2,2-trifluoroethoxy)methylsilane, tris(trifluoroacetoxy)methylsilane,
methyltriisocyanatosilane and combinations thereof.

17. The method of claim 1 wherein the porogen has a boiling point,
sublimation point or decomposition temperature ranging from about 150°C to
30 about 450°C.

18. The method of claim 1 wherein the step (c) crosslinking is conducted at a temperature which is less than the heating temperature of step (d).
- 5 19. The method of claim 1 wherein step (c) comprises heating the film at a temperature ranging from about 100 °C to about 250 °C, for a time period ranging from about 30 seconds to about 10 minutes.
- 10 20. The method of claim 1 wherein step (d) comprises heating the film at a temperature ranging from about 150 °C to about 450 °C, for a time period ranging from about 30 seconds to about 1 hour.
21. The method of claim 1 wherein the porogen has a molecular weight ranging from about 100 to about 50,000 amu.
- 15 22. The method of claim 1 wherein the porogen is selected from the group consisting of a polyalkylene oxide, a monoether of a polyalkylene oxide, a diether of a polyalkylene oxide, bisether of a polyalkylene oxide, an aliphatic polyester, an acrylic polymer, an acetal polymer, a poly(caprolactone), a
20 poly(valeractone), a poly(methyl methacrylate), a poly (vinylbutyral) and combinations thereof.
23. The method of claim 1 wherein the porogen comprises a polyalkylene oxide monoether which comprises a C₁ to about C₆ alkyl chain between oxygen
25 atoms and a C₁ to about C₆ alkyl ether moiety, and wherein the alkyl chain is substituted or unsubstituted.
24. The method of claim 23 wherein the polyalkylene oxide monoether is a polyethylene glycol monomethyl ether or polypropylene glycol monobutyl
30 ether.

25. The method of claim 1 wherein the porogen is present in the composition in an amount of from about 1 to about 50 percent by weight of the composition.

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26. The method of claim 1 wherein the composition further comprises a solvent.

27. The method of claim 1 wherein the composition further comprises solvent in an amount ranging from about 10 to about 95 percent by weight of the composition.

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28. The method of claim 1 wherein the composition further comprises a solvent having a boiling point ranging from about 50 to about 250°C.

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29. The method of claim 1 wherein the composition further comprises a solvent selected from the group consisting of hydrocarbons, esters, ethers, ketones, alcohols, amides and combinations thereof.

30. The method of claim 26 wherein the solvent is selected from the group consisting of di-n-butyl ether, anisole, acetone, 3-pentanone, 2-heptanone, ethyl acetate, n-propyl acetate, n-butyl acetate, ethyl lactate, ethanol, 2-propanol, dimethyl acetamide, propylene glycol methyl ether acetate, and combinations thereof.

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31. A nanoporous dielectric film produced on a substrate by the method of claim 1.

32. A semiconductor device comprising a nanoporous dielectric film of claim

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33. The semiconductor device of claim 32 that is an integrated circuit.
34. A composition comprising silicon containing pre-polymer, a porogen, and
5 a catalyst selected from the group consisting of onium compounds and
nucleophiles.
35. The composition of claim 34 wherein said catalyst is metal-ion-free.
- 10 36. The composition of claim 34 additionally comprising solvent.
37. The composition of claim 35 wherein said metal-ion-free catalyst is
tetramethylammonium acetate.
- 15 38. The composition of claim 34 wherein said silicon containing pre-polymer
comprises a combination of acetoxy-based leaving groups.
39. The composition of claim 38 wherein said combination of acetoxy-based
leaving groups comprises tetraacetoxysilane and methyltriacetoxysilane.
- 20 40. The composition of claim 34 wherein said porogen comprises polyethylene
glycol monomethylether.
41. The composition of claim 34 wherein said porogen comprises
25 polypropylene glycol dimethylether.
42. The composition of claim 34 wherein said porogen comprises
polyethylene glycol dimethylether.
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43. The composition of claim 34 wherein said porogen comprises polypropylene glycol monobutyl ether.
44. A precursor for stable nanoporous film formation comprising said composition of claim 35.
45. A spin-on composition comprising said composition of claim 35.
46. A film comprising said spin-on composition of claim 45.
47. A method of lowering the temperature at which a porous silica film forms comprising the step of adding onium ions or nucleophiles to a silicon-containing prepolymer and porogen.